

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08F 14/06, 4/34		A1	(11) International Publication Number: WO 00/17245
			(43) International Publication Date: 30 March 2000 (30.03.00)
<p>(21) International Application Number: PCT/EP99/06728</p> <p>(22) International Filing Date: 10 September 1999 (10.09.99)</p> <p>(30) Priority Data: 98203176.7 21 September 1998 (21.09.98) EP</p> <p>(71) Applicant (<i>for all designated States except US</i>): AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (<i>for US only</i>): VAN SWIETEN, Andreas, Petrus [NL/NL]; Reinaldstraat 6, NL-6883 HM Velp (NL). WESTMIJZE, Hans [NL/NL]; Burgemeester Boreelaan 1, NL-7437 BB Bathmen (NL). SCHUT, Jacobus [NL/NL]; Fonteinkruid 137, NL-7422 MV Deventer (NL).</p> <p>(74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Intellectual Property Dept. (Dept. AIP), P.O. Box 9300, NL-6800 SB Arnhem (NL).</p>			(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
<p>Published <i>With international search report.</i></p>			

(54) Title: CONTINUOUS DOSING OF VERY FAST INITIATORS DURING POLYMERIZATION REACTIONS

(57) Abstract

The invention pertains to a process wherein peroxides are dosed to a polymerization mixture, with essentially all of the organic peroxide that is used in the polymerization process having a half-life from 0.05 hour to 1.0 hour at the polymerization temperature. The dosing of such peroxide allows for accurate control of the polymerization rate, and the process will render a polymer with a low residual peroxide level.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

CONTINUOUS DOSING OF VERY FAST INITIATORS DURING
POLYMERIZATION REACTIONS

- 5 The present invention relates to a process to polymerize one or more monomers by means of one or more organic peroxides being dosed to the polymerization mixture at the reaction temperature.

Such a process is known from DE-OS-1 570 963. Herein it is taught to dose an 10 initiator, optionally mixed with a solvent, to the composition being polymerized via a stream of water. The organic peroxides that are exemplified in this patent application are peroxydicarbonates and acetyl-cyclohexyl-sulfonyl-peroxide (ACSP). They are used at a temperature of 54°C. The half-life of peroxydicarbonates at 54°C is known to vary from about 3.5 to 4.5 hours, depending on 15 the type of peroxydicarbonate used.

This process of DE-OS-1 570 963 was found to solve a number of problems in the industry. However, the process still suffers from insufficient control of the heat peak of the polymerization reaction, a related less than optimal use of the reactor, 20 a rather poor initiator efficiency, high residual peroxide levels in the resin produced, especially of the peroxydicarbonates, and/or the use of an undesirable initiator like ACSP which is known to lead, *inter alia*, to undesired fish eyes in the resin. A high residual peroxide concentration, especially of ACSP, is considered to correlate with a poor thermal stability of the resin containing it, which in turn is 25 associated with a discolouration of the resin upon further processing. Accordingly, a different process not suffering from these drawbacks is desired.

Similarly, EP-A-0 096 365 discloses how a peroxide is added in three parts during the polymerization. Again, difficulties in controlling the heat that is 30 subsequently generated are reported.

The current invention relates to a new process wherein these problems have largely been solved. More particularly, we have found that by selecting the proper organic peroxide and the proper dosing conditions, it is possible to obtain a polymerization reaction where the heat of polymerization is virtually constant over time, allowing optimum reactor space-time yield, very efficient peroxide usage, resulting in high polymer yields on the initiator, very low residual peroxide levels in the resin after polymerization, low fish-eye levels in the resin, and low reactor fouling. Accordingly, a resin with improved heat stability properties and low fish-eye levels was obtained, while the polymerization time could be shortened.

10

The new process is characterized in that essentially all of the organic peroxide used in the polymerization process has a half-life from 0.05 hour to 1.0 hour at the polymerization temperature. This allows for accurate control of the polymerization rate and related polymerization heat generation by controlling the peroxide dosing rate, while also resulting in a high yield of resin with low levels of residual peroxide and low fish-eyes.

The process according to the invention is pre-eminently suited to polymerize monomer mixtures comprising vinyl chloride monomer (VCM). Preferably, the process according to the invention involves the polymerization of monomer mixtures comprising at least 50% by weight (% w/w) of VCM, based on the weight of all monomer.

Comonomers that can be used are of the conventional type and include vinylidene chloride, vinyl acetate, ethylene, propylene, acrylonitrile, styrene, and (meth)acrylates. More preferably, at least 80% w/w of the monomer(s) being polymerized is made up of VCM, while in the most preferred process the monomer consists essentially of VCM. As is known in the art, the polymerization temperature of such processes to a large extent determines the molecular weight of the resulting resin.

30

In the process according to the invention, one or more peroxides may be used, as long as essentially all peroxides that are used fulfill the half-life requirement. It is noted that in JP-A-07082304 also a peroxide with a half-life within the range of 0.05-1.0 hour at polymerization temperature is dosed. However, according to this reference, another, more stable, peroxide is used from the start of the polymerization. This more stable peroxide does not fulfill the specified half-life requirement, and we have observed that the resulting resin contains an unacceptably high residue of this peroxide and, accordingly, will suffer from poor heat stability, which is typically observed in the form of discolouration during further processing of the resin.

Preferred examples of peroxides to be used in the process according to the invention are the following:

- 1,1,3,3-tetramethylbutylperoxy methoxy acetate, for polymerization reactions at 35-50°C, preferably 40-45°C.
 - diisobutanoylperoxide, bis(tert-butylperoxy) oxalate or 2,2-bis(2,2-dimethylpropanoylperoxy)-4-methyl pentane, for polymerization reactions at 40-65°C, preferably 45-60°C.
 - α-cumyl peroxyneodecanoate, 2-(2,2-dimethylpropanoylperoxy)-2-(2-ethylhexanoylperoxy)-4-methyl pentane or 2,4,4-trimethylpentyl-2-peroxyneodecanoate, at polymerization temperatures of 53-79°C, preferably 60-75°C, and
 - tert-amyl, tert-butyl peroxyneodecanoate or peroxydicarbonates, at polymerization temperatures of 58-87°C, preferably 75-80°C.
- Other peroxides may also be used. They can be classified into any of the above-mentioned categories on the basis of the 0.05 and 1.0 hour half-lives as determined by conventional thermal decomposition studies in monochlorobenzene, as well-known in the art (see for instance the brochure "Initiators for high polymers" with code 10737 obtainable from Akzo Nobel). As mentioned above, the process according to the invention requires that essentially

all peroxide be used at a polymerization temperature at which the half-life of the peroxide is from 0.05 hour to 1.0 hour. More preferably, essentially all peroxide that is used has a half-life of 0.05 to 0.8 hour, even more preferably 0.08 to 0.5 hour, most preferably 0.08 to 0.35 hour, at the polymerization temperature.

5

In a preferred embodiment, the invention relates to a process wherein the polymerization mixture is formulated at a temperature below the reaction (polymerization) temperature and subsequently heated to reach said desired reaction temperature. In such a cold-start process preferably at least 10 % by weight (%w/w), more preferably 20 to 40 %w/w, of the peroxide, based on the total weight of the peroxide used during the polymerization, is present at the start of the heating-up phase, while the remainder is dosed over a period of at least 1, preferably 2, and more preferably 2-4 hours, depending on the polymerization time. More preferably, the remainder of the peroxide is dosed from the time the reaction mixture temperature is controlled at the desired reaction temperature. The use of a small amount of peroxide from the start allows a fast heating up and start of the polymerization, since this peroxide will already (partly) decompose during the heating of the polymerization mixture. When the polymerization mixture reaches the polymerization temperature, the remainder of the peroxide can be dosed to the mixture to control the further polymerization rate. Preferably, the dosing is continuous, since this allows the most accurate control of the polymerization rate and a constant polymerization heat output, ensuring the highest efficiency and resin quality. The dosing time of 1-6 hours allows a very efficient use of the initiator. By using such dosing times, high yields of high-quality polymer were attained.

In another preferred embodiment, the reaction mixture is formulated at or near the polymerization temperature. In this process, hereinafter called warm-start process, it is not necessary to add a certain amount of peroxide at the start while the remainder is dosed over time. However, also in this warm-start process it can

be beneficial to add up to 20 %w/w of all peroxide immediately after formation of the reaction mixture, the remainder being dosed over time. Also in this warm-start process preferably at least 10 %w/w of all peroxide is present from the moment the reaction mixture reaches the desired reaction (polymerization) temperature. If 5 this procedure is used, the peroxide according to the invention preferably is added as the last ingredient. This procedure is particularly preferred if a certain amount of polymerization inhibitor (a radical trapping species) is present in the reaction mixture. If such a radical scavenger is present, for instance because it is introduced with the monomer wherein it is typically used as a stabilizer, the 10 initially dosed peroxide will react with said scavenger, thus preventing a delayed start of the polymerization reaction.

The amount of peroxide to be used in a process according to the invention is within the range conventionally used in polymerization processes. Typically, from 15 0.01 to 1 %w/w of peroxide, more specifically 0.01-0.5 %w/w, based on the weight of the monomer(s) to be polymerized, is used.

The peroxide is dosed to the reactor in the pure form or, preferably, in the form of a dilute solution or dispersion. One or more suitable solvents can be used to 20 dilute the peroxide. Preferably, such solvents are easily removed during the steps working up the polymer after the polymerization process, or they are of such a nature that it is acceptable to leave them as a residue in the final polymer. Furthermore, such solvents preferably do not adversely affect the thermal stability 25 of the peroxide dissolved therein, as can be verified by analyzing the half-life temperature of the peroxide in said solvent. An example of a suitable solvent is isododecane. If a peroxide dispersion is dosed, then the dispersion can be of either the peroxide itself or of a solution of the peroxide, preferably in said suitable solvents. Preferably, the dispersion is an aqueous dispersion. Preferably, the peroxide is dosed in a concentration of 1 to 50 %w/w, more preferably 1.5 to 30 25 %w/w, and most preferably 2 to 10 %w/w. The more dilute peroxide solutions

or dispersions ensure rapid mixing of the peroxide and the polymerization mixture, which leads to a more efficient use of the peroxide.

- The polymerization process can be conducted either as a mass process wherein
- 5 the reaction mixture is predominantly monomer or as a suspension process wherein the reaction mixture typically is a suspension of monomer in water, or as an emulsion or micro-emulsion process wherein the monomer typically is emulsified in water. In these processes the usual additives will have to be used. For example, if the monomer is present in the form of a suspension in water, the
- 10 usual additives like surfactant(s), protective colloid(s), anti-fouling agent(s), pH-buffer(s), etc. may be present. Depending on the type of polymer desired, each of the above-mentioned processes may be preferred. The process according to the invention is especially suited for mass and suspension processes.
- 15 After the polymerization, the resulting (co)polymer (or resin) will be worked up as is usual in the art. Polymers obtained by a suspension polymerization according to the invention, for example, will be submitted to the usual drying and screening steps. The resulting resin preferably is characterized in that it contains less than 50 ppm of residual peroxide, more preferably less than 40 ppm, and most
- 20 preferably, less than 25 ppm of peroxide, immediately after drying for 1 hour at 60°C and screening. The resin was found to exhibit excellent heat stability as measured with a Metrastat® PSD260 testing oven according to method ISO 182-2 (1990E). The improved heat stability proved that the resin hardly discoloured when submitted to melt-processing steps, e.g., to form shaped articles.

25

Experimental

- In a standard suspension polymerization experiment, a temperature controlled 5-
- 30 liter stainless steel Büchi reactor provided with one baffle, a three-bladed stirrer, a

pressure transducer, a VCM feed line, a nitrogen purge line, and a sampling line for taking samples from the gas phase, was charged with:

2600 g demineralized water,

1 g Na₂HPO₄ and 1 g NaH₂PO₄ buffer (ex Baker),

- 5 and pressurized to 15 barg, using nitrogen. If no leaks are observed, the reactor is evacuated and pressurized with nitrogen up to 5 barg three times to flush out virtually all air. If not all peroxide is dosed, then the desired amount of peroxide is added. Next, the reactor was evacuated and charged with 675 g VCM ex Akzo Nobel Salt & Basics and 3.4 g n-butane ex Praxair (first mixed with the VCM),
- 10 followed by heating up of the reactor, so that the reaction mixture was at the desired polymerization temperature after one hour. Ten minutes after starting the heating, a solution of 1.0125 g of Gohsenol KP-08 ex Nippon Gohsei in 100 g demineralized water was added to the reaction mixture. From this moment on the conversion was monitored by analyzing the gas phase of the reactor, as is known
- 15 in the art. After a pressure drop in the reactor, or 7.5 hours reaction time, whichever is shorter, the polymerization was continued for another half hour, and then the reactor was cooled to 20-25°C, evacuated and freed of virtually all remaining VCM. The polymer was obtained after filtration, washing, and drying (at 60°C for 1 hour using a fluidized bed).
- 20 The peroxides used, the amount dosed, and the polymerization results are presented in the following tables I-VII. The heat peak height correlates with the maximum slope of the conversion/time curve. The higher the heat peak, the more heat is being generated at a certain time and the more difficult it will be to control the temperature of the reaction mixture. A low heat peak together with high
- 25 polymer yields is preferred, since then an optimum in the space-time yield of the reactor can be attained. Unless specified otherwise, the peroxide is dosed from of the start of the heating up.

Table I

Example	1	A
Initiator	2,4,4-trimethylpentyl-2-peroxymethoxyacetate	
half-life at 42°C	0.21 hour	
Amount	0.1 %w/w on VCM	
Dosing form	Diluted with 100 g isododecane	n.r.
Added at start/dosed (weight ratio)	0/100	100/0
Dosing time (hours)	3	n.r.
Polymerization temperature (°C)	42	42
Heat peak height	55	20
Polymer yield(%)	90	Too low (<<90)

n.r. = not relevant

Table II

Example	2	3	B
Initiator	Diisobutanoyl peroxide (Trigonox 187-C30 ex Akzo Nobel)		
half-life at 57°C	0.1 hour		
Amount	0.1 %w/w on VCM		
Dosing form	diluted with 100 g isododecane	n.r.	
Added at start/dosed (weight ratio)	0/100	0/100	100/0
Dosing time (hours)	2	4	n.r.
Polymerization temperature (°C)	57	57	57
Heat peak height	74	78	5
Polymer yield(%)	80	90	46

Table III

Example	4	5	C
Initiator	2,4,4-trimethylpentyl-2-peroxy neodecanoate (Trigonox 423-C70 ex Akzo Nobel)		
half-life at 72°C	0.13 hour		
Amount	0.05 %w/w on VCM		
Dosing form	diluted with 100 g isododecane	n.r.	
Added at start/dosed (weight ratio)	0/100	0/100	100/0
Dosing time (hours)	0.17	4	n.r.
Polymerization temperature (°C)	72	72	72
Heat peak height	39	45	25
Polymer yield(%)	68	83	40

Table IV

Example	6	D
Initiator	Bis(tert.butylperoxy) oxalate	
half-life at 57°C	0.16 hour	
Amount	0.075 %w/w on VCM	
Dosing form	diluted with 100 g isododecane	n.r.
Added at start/dosed (weight ratio)	0/100	100/0
Dosing time (hours)	2	n.r.
Polymerization temperature (°C)	57	57
Heat peak height	75	18
Polymer yield(%)	79	Too low

Table V

Example	7	8	9	E
Initiator	Tert-butyl peroxyneodecanoate (Trigonox 23-C75 ex Akzo Nobel)			
half-life at 80°C	0.15 hour			
Amount	0.05 %w/w on VCM			
Dosing form	diluted with 100 g isododecane			n.r.
Added at start/dosed (weight ratio)	0/100	0/100	0/100	100/0
Dosing time (hours)	0.42	2	4	n.r.
Polymerization temperature (°C)	80	80	80	80
Heat peak height	29	67	57	43
Polymer yield(%)	58	77	87	66

Clearly, a proper selection of the dosing time influences the yield attainable. It was furthermore observed that in these trials, in which fouling of the reactor surface is typically noticeable, due to *inter alia* the high temperature of the reactor wall, less fouling was observed in the runs where the peroxide was dosed in 2 or 5 hours.

Table VI

Example	10	
Initiator	2,2-bis-(2,2-dimethylpropanoylperoxy)-4-methyl pentane	
half-life at 53°C	0.18 hour	
Amount	0.12 %w/w on VCM	
Dosing form	diluted with 100 g isododecane	n.r.
Added at start/dosed (weight ratio)	42/58	
Dosing time (hours)	1 hour after start of heat-up in 2 hours	
Polymerization temperature (°C)	53	
Heat peak height	39	
Polymer yield(%)	88	

Table VII

Example	11	F
Initiator	Trigonox 187-C30	di-2-ethylhexylperoxy dicarbonate (Trigonox EHP-C70) and Trigonox 187-C30
half-life at 57°C	0.1 hour	3.1 and 0.1 hour respectively
Amount	0.1 %w/w on VCM	0.06 %w/w on VCM
Dosing form	diluted with 100 g isododecane	
Added at start/dosed (weight ratio)	40/60	0.05 %w/w EHP at start 0.01 %w/w 187 dosed (83/17)
Dosing time (hours)	15 minutes after start of heat-up in 3 hours	2.5 hours after start of heat-up in 1 hour
Polymerization temperature (°C)	57	57
Heat peak height	34	45
Polymer yield(%)	81	90
Residual peroxide	<32 ppm*	150 ppm**

* = in final resin, as measured by iodometric titration on active oxygen, expressed as Trigonox 187, immediately after frying and screening.

** = in final resin, as measured by iodometric titration on active oxygen, expressed as Trigonox EHP, immediately after drying and screening.

Claims

1. Process to polymerize vinyl chloride monomer and optional further monomers using one or more organic peroxides, with at least part of the peroxide being dosed to the polymerization mixture at the reaction temperature, characterized in that essentially all of the organic peroxide used in the polymerization process has a half-life of from 0.05 hour to 1.0 hour at the polymerization temperature.
5
- 10 2. Process according to claim 1 wherein the peroxide dosed at the reaction temperature is dosed continuously.
- 15 3. Process according to claim 1 or 2 wherein at least 10 %w/w of the total amount of initiator is present at the start of the polymerization reaction, either before the reaction mixture is heated up to the desired reaction temperature, as in a cold-start process, or when the temperature of the reaction mixture is at said reaction temperature, as in warm-start processes.
- 20 4. Process according to claim 3 wherein 10-40 %w/w, more preferably 20-40 %w/w, of the total amount of peroxide is present at the start of the polymerization process.
- 25 5. Process according to any one of claims 1-4 wherein the peroxide, or the remainder of the peroxide, is dosed during a period of 1, preferably 2, and more preferably 4 hours, at the reaction temperature.
- 30 6. Vinylchloride based (co)polymer obtainable by any one of the processes of claims 1-5, having less than 50 parts by weight of residual peroxide, based on one million parts by weight of the (co)polymer, when measured

immediately after polymerization and drying of the (co)polymer for 1 hour at 60°C.

7. Use of a vinyl chloride (co)polymer according to claim 6 in a shaping process involving the heating of the co(polymer) to above its melting temperature.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/06728

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F14/06 C08F4/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 096 365 A (AIR PROD & CHEM) 21 December 1983 (1983-12-21) cited in the application abstract; claims; examples page 14, line 1 - line 8 ---	1-7
X	DATABASE WPI Section Ch, Week 9602 Derwent Publications Ltd., London, GB; Class A14, AN 96-017232 XP002093830 & JP 07 292018 A (NIPPON OILS & FATS CO LTD), 7 November 1995 (1995-11-07) abstract --- -/-	1-7

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

21 December 1999

Date of mailing of the international search report

12/01/2000

Name and mailing address of the ISA -

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Mettler, R-M

INTERNATIONAL SEARCH REPORTInternational Application No
PCT/EP 99/06728

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 492 712 A (AKZO NV) 1 July 1992 (1992-07-01) abstract; claims; examples 19,23 page 3, line 19 - line 27 -----	1-7
X	EP 0 717 035 A (SHINETSU CHEMICAL CO) 19 June 1996 (1996-06-19) abstract; claims; example 4 page 5, line 1 - line 12 -----	1-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/06728

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 0096365	A	21-12-1983	JP	59001516 A		06-01-1984
JP 7292018	A	07-11-1995		NONE		
EP 0492712	A	01-07-1992	CA	2058347 A		25-06-1992
			JP	4318002 A		09-11-1992
EP 0717035	A	19-06-1996	DE	69509051 D		20-05-1999
			DE	69509051 T		23-09-1999
			JP	8225521 A		03-09-1996
			US	5783647 A		21-07-1998
			JP	8225613 A		03-09-1996